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(54) Title: INHIBITION OF BACTERIAL GROWTH

(57) Abstract

The invention provides a means of inhibiting bacterial growth particularly on a coated substrate. It comprises a method of forming a substantially dry powder coating composition containing a biocide, applying the powder coating composition to form a coating on the substrate, the biocide being capable of retaining effective biocidal activity in the coating.

INHIBITION OF BACTERIAL GROWTH

This invention relates to the inhibition of bacterial growth and particularly to the inhibition of bacterial growth on a substrate.

It is an object of the invention to provide a method of inhibiting bacterial growth when a coating composition is applied to a substrate.

It is also an object of the invention to provide a coating composition for use in the method of the invention.

In one aspect the invention provides a method of inhibiting the growth of bacteria on a substrate, the method comprising forming a substantially dry powder coating composition containing a biocide, applying the powder coating composition to form a coating on the substrate, the biocide being capable of retaining effective biocidal activity in the coating.

Preferably the composition is applied to the substrate by spraying by electrostatic or tribocharge means.

In another aspect the invention provides a coating composition for use in the method of the immediately preceding paragraph, the composition containing 0.1 to 20% by weight of a biocide, the powder being substantially dry and being adapted for application to a substrate by electrostatic or tribocharged spraying. Preferably the biocide is present in an amount of from 0.1 to 10% by weight.

The invention also provides a coated article made by the method of and/or comprising a coating according to the present invention.

In one embodiment the invention provides a powder mixture comprising a biocide powder and a powder or powders to form the matrix of the coating composition.

In this embodiment the biocide will conveniently have the same physical characteristics as the matrix powder for ease of application.

Alternatively, the biocide may be incorporated in the powder to form the matrix of the coating. Whichever method is used, it is desirable that the biocide be homogeneously mixed throughout the powder composition. In practice, this may for example be achieved during manufacture of the powder composition. The final powder, therefore, in one preferred embodiment, has particulates each of which contains biocide, matrix powder and any other included ingredients. As each particulate contains the biocide it is homogeneously distributed throughout the coating composition and so cannot separate out. Thus, for example, such a powder may be made by adding the biocide at the initial mixing stage of the constituents which are to be converted into the desired matrix powder. In a typical powder manufacturing process, the precursors of the desired powder, e.g. the resin base and its hardener, together with any other additives, are mixed, heated and extruded to sheet form, the sheet is granulated and then ground to the desired powder size. Excellent mixing of the constituents is thereby achieved and all the constituents in the desired proportions are present in each of the individual particles of the final powder.

The coating composition preferably includes pigments and the powder to form the matrix of the coating composition, therefore, includes in this embodiment suitable pigmentation.

The coating composition is preferably formed as a dry mixture of the powder constituents.

The biocide may be selected to be active against Gram positive and/or Gram negative bacteria, algae, filamentous fungi or yeasts and may be a general purpose biocide that is active against more than one such category.

Many biocides may be suitably employed in the invention and the average skilled man of the art will readily be able to determine by routine experimentation whether the biocidal activity of any particular biocide will be sufficiently retained for his particular needs in the coating. The necessary criteria are that the biocide can be provided in a suitable powder form and that it can survive the coating process.

Particularly suitable classes of biocides have been found to include:

trichloro hydroxy diphenyl ethers, e.g. 2,4,4^1 - trichloro - 2^1 - hydroxy diphenyl ether,

methyl ureas, e.g. 3.- (3,4 - dichlorophenyl) - 1,1 - dimethyl urea,

imidazolcarbamates.

The matrix of the coating composition may be provided by any suitable material that can be manufactured in powder form, gives the desired properties, e.g. durability, to the applied coating and bonds satisfactorily to the substrate surface.

The article to which the coating is applied is preferably metal, although the invention is not limited thereto and includes, for example, domestic appliances (so-called white and brown goods), work surfaces for domestic and industrial use, architectural and other

engineering products, such as hand rails, door handles and plates; garden furniture; and the like. Typical substrates may be, for example, ferrous metals, zinc-coated steels, aluminium and the like. The article may thus be used in any environment where hygiene is advantageous.

The powdered coating compositions of the invention may be applied, as indicated above, by electrostatic spraying which may be manual or automatic, or by tribocharged spraying.

Particularly suitable materials to form the matrix of the coating composition include epoxy, polyesters and epoxy-polyesters and are available in powder form, pre-pigmented and to provide a variety of desired surface finishes - gloss, matt and textured. However, the invention is not so limited and is also applicable to the use of other polymeric powder materials, e.g. thermoplastic materials, e.g. nylon, acrylics, polyethylene, polypropylene and eva.

Typically the matrix powders may have a specific gravity of from 1.2 to 1.9 and a particle size of which 100% is less than 100 microns and 40 to 60% is greater than 34 microns. They may have stoving temperatures, for example, of at least 120°, e.g. 140° to 210°C depending, of course, as the physical characteristics of the specific material used.

The biocide, when used as a separate powder, is preferably chosen to have a similar particle size distribution to that of the matrix powder.

The amount of biocide incorporated in the powder composition will vary depending on the intended end use and the strength and nature of the particular biocide. Thus suitable amounts can readily be determined from the known mic values of the particular biocide. For example, up to 20% by weight of biocide based on the total

powder composition may be used. Typically useful proportions are from 0.1 to 10% by weight of the total powder composition, especially from 2 to 6% by weight.

Other ingredients may be included in the powder composition, for example fluidity agents, dispersants, preservatives.

The powder mixture incorporating the biocide powder has good shelf life depending on the particular biocide used but, alternatively, may be mixed shortly prior to use.

As is well appreciated in the coating art, the substrate must be thoroughly clean before application of the powder mixture and cleaning, e.g. by shot-blasting and/or chemical means may be carried out by conventional means.

Specific embodiments of the invention are further described in the following Examples:

Example 1

Pigmented powdered coating compositions were made by mixing the following powder materials in the proportions shown

		Parts by weight
BIOCIDE	-	0 to 6
Matrix powder	-	100 to 94

The BIOCIDE was a 2,4,4^{1} - tricholoro - 2^{1} hydroxy diphenylether supplied by CIBA GEIGY as IRGASAN DP 300. The matrix powder was a proprietory polyester powder.

The powdered mixture was sprayed electrostatically onto one metal surface which had previously been degreased shot-blasted to provide several sample slides coated on one surface only.

Bacterial lawn plates of five different bacteria, as listed in Table 1 below, in Tryptone Soya Agar were prepared and a sample slide was placed, coated side down, in the centre of each plate. The plates were incubated at 37°C for 24-48 hours and observed for zones of inhibition.

The results are listed in Table 1 below, being based on 3 replicates per slide:

TABLE 1

Organism	**Percentage of Biocide**			
	O	2	4	6
E.Coli	---	+--	+--	+---
P.aeruginosa	---	+--	+--	+--
S.typhimurium	---	---	---	---
S.aureus	+--	+--	+--	+--
S.faecalis	---	---	+--	---

+-- = indicates inhibition

--- = no inhibition

Example 2

A powdered coating composition was made by mixing the following powder materials in the proportions shown.

	Parts by weight
BIOCIDE	6
Matrix powder	94

The BIOCIDE was as in Example 1.

The matrix powder was a polyester supplied by H B Fuller Coatings Limited, Birmingham, England under the identification OMEGA PC P6/035.

The powder mixture was sprayed on to microscope glass slides of about 25mm width at a temperature of 200°C for five minutes.

Bacterial lawn plates of eight different bacteria, as listed in Table 2 below, were prepared as follows. The coated slides were placed, coated face upwards in Petri dishes containing Agar nutrient as for Example 1. A thin film of the nutrient covered the test slides. Each bacteria was applied in a line across a dish and continuing over the test slide. As before, a set of three samples were tested in each instance, i.e. in each Run.

In Table 2 are listed the Degree of Inhibition (DOI) and the Zone of Inhibition (ZOI) in mm. The DOI indicates the amount of the width of each line of bacteria that disappeared and the DOI indicates the amount of the length of the line of organisms across and on either side of its slide that disappeared.

	Run 1		Run 2	
Organism	**DOI**	**ZOI(mm)**	**DOI**	**ZOI(mm)**
Staphylococcus aureas (Oxford)	Complete	55	Complete	55
Staphylococcus aureas (Resistant)	Complete	50	Complete	45
Enterococcus faecalis	50%	25	50%	25
Escherichia-coli	Complete	30	Complete	30
Salmonella typhimurium	Complete	30	Complete	30
Pseudomonas aeruginosa	NIL	-	NIL	-
Corynebacterium diptheria (non-toxic)	50%	25	50%	25
Bacillus subtilis	Complete	35	Complete	35

Example 3

Example 2 was repeated but using the six organisms listed in Table 3 below and using biocide concentrations of from 0 to 20% by weight. The Zones of Inhibition were again measured and are listed in Table 3.

TABLE 3

Organism	Biocide concentration (%w/w)				
	0	6	10	15	20
E.coli	0	31	43.7	57.3	49.3
Strep faecalis	0	25	25	25	26.7
S. aureas (Oxford)	42	52.3	76.7	100	100
S aureas (Resistant)	42.3	53.7	100	100	100
P. aeruginosa	0	0	0	0	0
B. subtilis	0	26	32	41.6	43
Salmonella typhimurium	0	25.3	32	39	43

It will be appreciated that the invention is not limited to the specific embodiments described. For example, another suitable technique for applying the coating to a metal substrate is the so-called plastics coating technique in which the substrate is preheated and dipped into a bed of the powder. Such a technique also forms part of this invention.

CLAIMS

1. A method of inhibiting the growth of bacteria on a substrate, the method comprising forming a substantially dry powder coating composition containing a biocide, applying the powder coating composition to form a coating on the substrate, the biocide being capable of retaining effective biocidal activity in the coating.

2. A method according to Claim 1, in which the composition is applied to the substrate by spraying by electrostatic or tribocharged means.

3. A method according to Claim 1 or 2, wherein the biocide is a powder and is mixed with a powder coating composition.

4. A method according to Claim 1 or 2, in which the biocide is mixed with the precursors of the powder or powders which are to form the matrix of the powder coating composition.

5. A method according to any preceding Claim, in which pigmentation is mixed into the powder coating composition.

6. A method according to any preceding Claim, wherein the coating is applied to the substrate using a stoving temperature of 140^0 to 210^0C.

7. A method according to any preceding Claim, wherein the coating composition is applied to a metal substrate.

8. A method according to any preceding Claim, wherein the biocide is incorporated in the powder coating composition in an amount of from 0.1 to 20% by weight.

9. A method according to Claim 8, wherein the biocide is incorporated in the powder coating composition in an amount of from 2 to 6% by weight.

10. For use in the method of any preceding Claim, a powder coating composition containing 0.1 to 20% by weight of a biocide, the powder being substantially dry and being adapted for application to a substrate by electrostatic or tribocharged spraying or by dipping the preheated substrate.

11. A powder coating composition according to Claim 10, wherein the biocide is present in an amount of from 2 to 6% by weight.

12. A powder coating composition according to Claim 10 or 11, wherein the biocide and the matrix of the coating composition are powders of substantially the same physical characteristics.

13. A powder coating composition according to Claim 10, 11 or 12, wherein the biocide is a trichloro hydroxy diphenyl ether.

14. A powder coating composition according to Claim 10, 11 or 12, wherein the biocide is 2,4,4^{1} - trichloro - 2^{1} - hydroxy diphenyl ether.

15. A powder coating composition according to Claim 10, 11 or 12, wherein the biocide is a methyl urea.

16. A powder coating composition to claim 15, wherein the biocide is 3 - (3,4 - dichlorophenyl) - 1,1 - dimethyl urea.

17. A powder coating composition according to Claim 10, 11 or 12 wherein the biocide is an imidazolcarbamate.

18. A powder coating composition according to any one of Claims 10 to 17, which comprises a polyester or epoxy polyester powder.

19. A powder coating composition according to any one of Claims 10 to 18, which comprises a thermoplastic powder, e.g. of nylon

20. A powder coating composition according to any one of Claims 10 to 19, which comprises a matrix powder of specific gravity from 1.2 to 1.9 and a particle size less than 100 microns.

21. A powder coating composition according to any one of Claims 10 to 20, in which the particulates of the powder each contain the biocide.

22. An article comprising a substrate having a coating applied by the method of any one of Claims 1 to 9 or as defined in any one of Claims 10 to 21.

INTERNATIONAL SEARCH REPORT

Interr ıal Application No
PCT/GB 96/01374

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C09D5/14 C09D5/03

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 96, no. 7 & JP,A,08 060036 (NIPPON ESTER CO LTD) see abstract ---	1,3,4, 8-11,18, 22
X	DATABASE WPI Section Ch, Week 9409 Derwent Publications Ltd., London, GB; Class A82, AN 94-072114 XP002024460 & JP,A,06 025 561 (TOA GOSEI CHEM IND LTD) , 1 February 1994 see abstract --- -/--	1,3, 7-11,19, 22

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
4 February 1997	11.02.97
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl, Fax (+ 31-70) 340-3016	Authorized officer Girard, Y

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PCT/GB 96/01374

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US,A,3 817 762 (LOREN D. BRAKE) 18 June 1974 see column 5, line 34-73 see column 5, paragraph 2 see abstract	1-3,5,7, 8,10,22
X	DATABASE WPI Section Ch, Week 9413 Derwent Publications Ltd., London, GB; Class A23, AN 94-106899 XP002024461 & JP,A,06 057 032 (TOA GOSEI CHEM IND LTD) , 1 March 1994 see abstract	1,10,19, 22
A	US,A,3 988 294 (HARRY ELWYN HILL) 26 October 1976 see abstract	15,16
A	FR,A,2 409 250 (CIBA-GEIGY) 15 June 1979	13

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

Inter nal Application No
PCT/GB 96/01374

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
US-A-3817762	18-06-74	NONE		
US-A-3988294	26-10-76	CA-A-	1029299	11-04-78
		DE-A-	2510330	23-10-75
		FR-A-	2264067	10-10-75
		GB-A-	1474664	25-05-77
		JP-A-	50125029	01-10-75
FR-A-2409250	15-06-79	LU-A-	78554	13-06-79
		AR-A-	223154	31-07-81
		DE-A-	2849856	23-05-79
		GB-A,B	2010260	27-06-79
		JP-A-	54084535	05-07-79
		US-A-	4339462	13-07-82
		US-A-	4268693	19-05-81